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# CHRONOPOTENTIOMETRY OF REFRACTORY METALS, ACTINIDES AND OXYANIONS IN MOLTEN SALTS: A REVIEW

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## ABSTRACT

The applications of chronopotentiometry to the study of electrochemical behavior of three technologically important areas of refractory metals, actinides, and oxyanions in molten salts are critically reviewed. Chronopotentiometry is a very versatile diagnostic tool to understand the reaction mechanism of the electrode processes for the electrochemical reduction/oxidation of these electroactive species in molten salt solutions. Well adherent, compact, and uniformly thick coatings of refractory metals may be electrodeposited from their solutions in molten salts.

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## 1. INTRODUCTION

Chronopotentiometry is an electrochemical technique in which a dilute unstirred solution of an electroactive species, in the presence of an excess of a supporting electrolyte, is subjected to a constant current electrolysis and the variations of the working electrode potential, against a suitable non-polarizable reference, are recorded as a function of time. The resulting potential-time curve is known as the chronopotentiogram. A schematic circuit diagram for chronopotentiometry is given in Fig. 1. A typical chronopotentiogram is shown in Fig. 2. The time elapsed between the onset of electrolysis and when the depolarizer concentration at the electrode surface becomes zero is called the transition time. When the mass transport is controlled by semi-infinite linear diffusion, the transition time,  $\tau$ , is given by the Sand equation:

$$\tau^{1/2} = \pi^{1/2} n F A C^0 D^{1/2} / 2I$$

where  $n$  is the number of electrons involved in the electrode process,  $F$  is the Faraday constant,  $A$  is the area of the indicator electrode,  $C^0$  is the depolarizer bulk concentration in solution,  $D$  is the diffusion coefficient, and  $I$  is the constant electrolysis current. For a diffusion-controlled process, the Sand equation predicts that the product  $I\tau^{1/2}$  should be a constant and proportional to the depolarizer bulk concentration. The Sand equation is applicable to both reversible and irreversible electrode processes.

For a reversible electrode process in which the reaction product is soluble in either the solution or the electrode, the potential-time relation is given by

$$E = E_m + RT/nF \ln[(\tau^{1/2} - t^{1/2})/t^{1/2}]$$

where  $E$  is the electrode potential at time  $t$ ,  $R$  is the gas constant,  $T$  is the temperature in Kelvin, and  $E_m$  is called the quarter-wave potential which corresponds to one-fourth the

transition time. For an irreversible, diffusion-controlled process, the potential-time relation is given by

$$E = RT/\alpha nF \ln(\tau^n - t^n) + RT/\alpha nF \ln[2k_f/(\pi D)^{1/2}]$$

where  $\alpha$  is the transfer coefficient, and  $k_f$  is the heterogeneous rate constant. In the irreversible case the  $E_m$  varies with the amount of the applied current and the depolarizer bulk concentration.

Chronopotentiometry is a very useful diagnostic technique to study the electrochemical behaviour of molten salt solutions. It has several intrinsic advantages over other electrochemical methods applicable in such media (1, 2). An electrode reaction can be studied in both directions by simple reversal of the current at the chronopotentiometric transition time. Complications due to secondary effects such as adsorption often can be more adequately taken into account in chronopotentiometric studies. When the electroactive species is adsorbed on the electrode,  $i\tau^n$  increases with increase in current. Chemical reactions coupled to the electron transfer step can also be easily investigated by chronopotentiometry. For example, when a chemical reaction precedes the electron transfer process,  $i\tau^n$  is not a constant, but decreases with increase in current.

Chronopotentiometry was first applied (3) to fused salt systems to study the reduction of Bi(III), Ag(I), Cu(I) and Cd(II) in molten LiCl-KCl eutectic at 450 °C using platinum microelectrodes. The present paper is a review of the applications of this technique to the study of reaction mechanisms in three areas of technological and academic significance: refractory metals, actinides, and oxyanions. Some other related areas have been reviewed (1, 2, 4-18), as have values of diffusion coefficients (19, 20) measured by different techniques including chronopotentiometry, and are not discussed here. Theory and instrumentation are not included as these have been the subject matter of earlier reviews (21-31). The notation LiCl-KCl here means the eutectic composition; NaCl-KCl means the

equimolar mixture; and FLINAK means the 46.5-11.5-42.0 mol% LiF-NaF-KF mixture.

## **2. THE REFRACTORY METALS**

The elements of Groups IVB, VB, and VIB of the periodic table are conveniently called the refractory metals. Chronopotentiometry has found applications in the study of electrodeposition of coherent deposits of refractory metals from solutions in fused electrolytes.

**2.1. Titanium.** The electrochemical oxidation of Ti(II) added as  $\text{Ti}(\text{AlCl}_4)_2$  in  $\text{AlCl}_3$ -NaCl (65:35 to 52:48 mol %) melts at platinum and gold electrodes has been studied (32) in the temperature range 150-330 °C using chronopotentiometry, current-time curves and linear sweep voltammetry. Ti(II) is oxidized stepwise to Ti(III) and Ti(IV), both steps being electrochemically reversible at platinum electrodes. The lower oxidation states were more stable at lower temperatures and in melts of higher  $\text{AlCl}_3$  content. This is because low oxidation states of metals, which are usually more basic than the higher oxidation states, are stabilized through the formation of an acid-base adduct with the strongly acidic  $\text{AlCl}_3$ -containing solvents. Weak adsorption of Ti(II) at platinum has been indicated.

The electrochemical reduction of Ti(IV) in molten  $\text{NaBF}_4$  (33) at 420 °C and molten FLINAK (34) at 500 °C have been investigated by chronopotentiometry, voltammetry and chronoamperometry. The reduction of Ti(IV) to Ti(III) was reversible at platinum and pyrolytic graphite electrodes in both melts. No further reduction steps could be observed in  $\text{NaBF}_4$ . In FLINAK, on the other hand, further reduction of Ti(III) to Ti(0) was seen to be a reversible process involving alloy formation with the platinum electrode. The electrochemical oxidation of Ti(III) to Ti(IV) at unsheathed platinum and sheathed glassy carbon electrodes was reversible (34) in molten  $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$  (65.6-29.4-5.0 mol %) at 500° C as studied by chronopotentiometry and voltammetry. The electrode potential of the Ti(IV)/Ti(III)

couple was more anodic in  $\text{LiF-BeF}_2\text{-ZrF}_4$  than in FLINAK, showing the higher Lewis acidity of the former melt.

**2.2. Zirconium.** Electrodeposition of zirconium on a molybdenum electrode from a solution of  $\text{ZrCl}_4$  in  $\text{NaCl-KCl}$  at  $770^\circ \text{C}$  has been studied (35) by chronopotentiometry. The average oxidation state of ionic zirconium was 2.25. Temperature dependence of the diffusion coefficient of  $\text{Zr(II)}$  was Arrhenian which was confirmed by Sakakura (36), who also measured the diffusion coefficient of  $\text{Zr(IV)}$  in this melt.

Insoluble  $\text{ZrCl}_3$  is formed (37) on the electroreduction of  $\text{Zr(IV)}$  in molten  $\text{AlCl}_3\text{-NaCl}$  (51-52 mol %  $\text{AlCl}_3$ ) at  $175\text{-}220^\circ \text{C}$ . The reduction process involves nucleation overpotential as indicated by maxima in chronoamperometric current-time curves, potential overshoots in chronopotentiometric measurements, and a large anodic shift of the peak potential in subsequent cyclic voltammograms. Reduction of  $\text{Zr(IV)}$  in very acidic  $\text{AlCl}_3\text{-NaCl}$  (60 mol %  $\text{AlCl}_3$ ) at temperatures higher than  $250^\circ \text{C}$  gives  $\text{Zr(II)}$  and soluble  $\text{Zr(III)}$ ; the latter probably disproportionates to  $\text{Zr(II)}$  and  $\text{Zr(IV)}$  at temperatures lower than  $140^\circ \text{C}$ . The Raman spectrum of  $\text{ZrCl}_3$  was also reported in this work.

From a chronopotentiometric study of  $\text{ZrF}_4$  in molten FLINAK between  $500$  and  $750^\circ \text{C}$ , Mellors and Senderoff (38) found the deposition of zirconium to be a single, irreversible, four-electron reduction step. However, from polarographic measurements in  $\text{LiF-NaF-KF-ZrF}_4$  at  $500^\circ \text{C}$ , the single four-electron step reduction was suggested (39) to be reversible. The electroreduction of  $\text{Zr(IV)}$  from a solution of  $\text{ZrF}_4$  in  $\text{NaCl}$  occurred (40) in a single, irreversible, four-electron step, in agreement with the findings of Mellors and Senderoff.

**2.3. Hafnium.** From a study (41) of the electroreduction of  $\text{HfCl}_4$  in  $\text{NaCl-KCl}$ , the electrode reaction  $\text{Hf(II)} + 2e \rightarrow \text{Hf}^0$  was found to be diffusion controlled, the optimum plating temperature being  $830\text{-}850^\circ \text{C}$ . The experimental value of the diffusion coefficient of  $\text{Hf(II)}$  was in good agreement with that calculated

from the Stokes-Einstein equation. At temperatures between 700-750° C and mole fractions of HfCl<sub>4</sub> less than 10<sup>-3</sup>, the reduction of Hf(IV) in NaCl-KCl on a tungsten electrode proceeded (42) in three steps:  $\text{Hf(IV)} + e \rightleftharpoons \text{Hf(III)}$ ;  $\text{Hf(III)} + e \rightleftharpoons \text{Hf(II)}$ ;  $\text{Hf(II)} + 2e \rightleftharpoons \text{Hf(O)}$ . At 850-900° C, the reduction occurred in two steps:  $\text{Hf(IV)} + 2e \rightleftharpoons \text{Hf(II)}$ ;  $\text{Hf(II)} + 2e \rightleftharpoons \text{Hf(O)}$ .

**2.4. Vanadium.** In LiCl-KCl at 450° C Vanadium(V) added as V<sub>2</sub>O<sub>5</sub> was reduced (43) to a mixed lithium vanadium oxide (lithium vanadium bronze) on the pyrolytic graphite electrode surface at a potential which was a function of the solute concentration. The ratio of V<sub>2</sub>O<sub>4</sub>:V<sub>2</sub>O<sub>5</sub> in the insoluble reduction product formed on the electrode surface was within the limits of 1:2 to 1:3.

Scrosati and Laitinen (44) used chronopotentiometry and current reversal chronopotentiometry to study the electrochemistry of VO<sup>2+</sup>, added as vanadyl sulphate, in the same melt. Three reduction steps were observed of which only the first step followed the Sand equation. VO<sup>2+</sup> was reduced to VO<sup>+</sup> which underwent a rapid and irreversible chemical reaction to give V<sub>2</sub>O<sub>3</sub> and V<sup>3+</sup>.

Electroreduction of V(V) to V(IV) in molten equimolar NaPO<sub>3</sub>-KPO<sub>3</sub> at 700° C is reported (45) to be a single, one-electron step, quasi-reversible process. The product V(IV) is non-electroactive in this melt. Diffusion coefficients of V<sup>+</sup> in molten K<sub>2</sub>SO<sub>4</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> have been determined (46) in the temperature interval 390-460° C using chronopotentiometry and chronoamperometry.

**2.5. Niobium.** Electrolytic reduction of Nb<sub>3</sub>Cl<sub>8</sub> in several molten alkali metal chlorides has been investigated (47) by chronopotentiometry and coulometry. The reduction of Nb<sub>3</sub>Cl<sub>8</sub> to Nb<sup>0</sup> occurred in two steps, independent of the melt composition. The first step was a diffusion controlled, reversible, two-electron reaction:  $\text{Nb}_3\text{Cl}_8 + 2e \rightleftharpoons 3\text{NbCl}_2 + 2\text{Cl}^-$  which was followed by an irreversible process:  $\text{NbCl}_2 + 2e \rightarrow \text{Nb}^0 + 2\text{Cl}^-$  which was not diffusion controlled. Temperature dependence (48) of the



diffusion coefficients of Nb(III) in molten LiCl-KCl was Arrhenian. However, these results did not obey the Stokes-Einstein equation unless a correction factor was introduced.

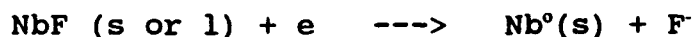
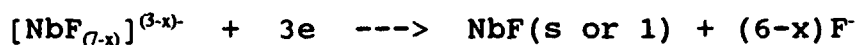
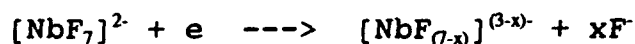
Electroreduction of niobium has been studied (49) in LiCl-KCl at 720° C and NaCl-KCl at 760° C. No reduction wave could be obtained for Nb(III) in contrast to the report of Pimenov and Baimakov (48), but the higher valent niobium ions were found to be electroactive. The reduction process was a reversible, one electron step with the product soluble in the melt and was ascribed to reduction of tetravalent niobium:  $\text{Nb(IV)} + e \rightarrow \text{Nb(III)}$ . The reduction waves did not obey the Sand equation; transition times decreased with time, probably because of the volatilization of niobium chloride out of the system. Electroreduction of  $\text{K}_2\text{NbF}_7$  on a molybdenum electrode in NaCl-KCl has been investigated (50, 51) using chronopotentiometry, voltammetry, and controlled potential and controlled current coulometry. The reduction proceeded in two steps. The first step was a diffusion controlled, reversible, two-electron process giving a product soluble in the bath. The second step was an irreversible process forming metallic niobium as the reduction product. Temperature dependence of the diffusion coefficients of Nb(II) and Nb(III) in NaCl-KCl followed (48) the Arrhenius equation, but the Stokes-Einstein equation was not obeyed.

From a study (49) of the electroreduction of niobium in KCl-CsCl (70-30 mol %) at 760° C and equimolar KCl-CsCl at 750° C, Nb(III) was found to be non-electroactive while higher valent niobium ions were electroactive. The reduction step was reversible involving a single electron, the product being soluble in the melt, and was ascribed to the reduction of tetravalent niobium:  $\text{Nb(IV)} + e \rightarrow \text{Nb(III)}$ . The Sand equation was found to be obeyed only in the less polarising equimolar KCl-CsCl melt. For the reduction of Nb(IV) in LiCl-KCl and NaCl-KCl the Sand equation was not applicable (*vide supra*).

The electroreduction of Nb(V) on platinum and tungsten electrodes has been studied (52) in  $\text{AlCl}_3$ -NaCl melts of different compositions using chronopotentiometry, chronoamperometry,

linear sweep voltammetry, and differential pulse polarography. The reduction mechanism was dependent on the Lewis acidity of the melt which in turn was determined by the working temperature and the solvent composition. In  $\text{AlCl}_3\text{-NaCl(satd.)}$  melt, four reduction steps were observed from all the techniques, particularly at low current densities (chronopotentiometry) and slow scan rates (linear sweep voltammetry). Only the first step was essentially a single-electron, diffusion-controlled, reversible process. At longer times, the reduction mechanism was of the ECEEE type where E represents an electron transfer step and C denotes a coupled chemical reaction. The chemical step following the first reduction process is probably the dimerization of  $\text{Nb(IV)}$ . At faster scan rates or shorter times, the effect of the dimerization step was no longer observed and the first two reduction steps were simple reversible electrode processes each involving one electron. Temperature dependence of the diffusion coefficients of  $\text{Nb(V)}$  could be expressed by an Arrhenius equation in the temperature range 160-300 °C. The reduction scheme for  $\text{Nb(V)}$  was the same in both melts containing 45 or 37 mole %  $\text{NaCl}$ , but different from the one described above. Deposition of niobium metal was not observed in any of these melts.

Electrodeposition (53) of Nb from a solution of  $\text{K}_2\text{NbF}_7$  in FLINAK proceeded in three reduction steps:



the first two of which were reversible and diffusion controlled.

**2.6. Tantalum.** The electrolytic reduction and oxidation of  $\text{TaCl}_5$  in  $\text{LiCl-KCl}$  have been studied (54) by chronopotentiometry and coulometry between 500 and 675° C. Cathodic chronopotentiograms

showed two reduction waves. From current reversed cathodic-anodic chronopotentiograms it was concluded that the first step corresponds to a diffusion controlled, reversible, two-electron reduction of Ta(IV) [in the form of a complex anion, probably  $[\text{TaCl}_6]^{2-}$  to Ta(II) and the second step was an irreversible reduction of Ta(II) to tantalum metal. The anodic chronopotentiogram showed only one oxidation wave. The current reversal anodic-cathodic chronopotentiograms indicate that this step corresponds to a diffusion controlled, reversible one-electron oxidation of Ta(IV) to Ta(V). The Ta(V) in this melt probably exists as a complex anion,  $[\text{TaCl}_6]^-$ .

It is not certain (55) whether the reduction studies of Suzuki involved only the Ta(IV) state. Anodization (55, 56) of tantalum metal in LiCl-KCl produces a mixture of oxidation states, Ta(V), Ta(IV) and a lower (probably Ta(II)) state. Ta(V) was volatile at the experimental temperature of 450 °C. The spectroscopic studies showed that Ta(V) is present as  $[\text{TaCl}_6]^-$  in the melt, in agreement with Suzuki's results (54). The anodized products were studied using voltammetry, cyclic voltammetry, and chronopotentiometry. Ta(V) is reversibly reduced to Ta(IV) which in turn reduces directly to the metal in contrast to Suzuki's observations (54). Ta(II) is also reduced directly to the metallic state. Reduction behaviour of Ta(V) in molten chlorides is quite different from that in fluorides melts (57) where the reduction proceeds in two steps; a three electron process followed by a two electron step and the tetravalent state is not observed.

Electrochemical reduction of  $\text{K}_2\text{TaF}_7$  in NaCl-KCl at 720 °C, as studied (57A) by chronopotentiometry and cyclic voltammetry, involved a single reversible step  $\text{Ta(V)} + 5\text{e} \rightleftharpoons \text{Ta}$ . In the presence of added NaF, the deposition potential shifted to more negative values probably due to the formation of increasing amounts of complex species such as  $[\text{TaF}_7]^{2-}$  or  $[\text{TaF}_8]^{3-}$ . Diffusion coefficient of the complex species containing Ta(V) was determined to be  $\sim 1.5 \times 10^{-5} \text{ cm}^2/\text{sec}$  from chronopotentiometry and cyclic voltammetry.

Electrochemistry of tantalum has been studied (58) in molten CsCl-KCl(60:40 mol %) employing chronopotentiometry, cyclic voltammetry, and potentiostatic techniques. Tantalum ions in solutions were generated by anodization of tantalum metal. The reduction of tantalum ions occurred through one main process, the products being tantalum metal and an unidentified solid. The nature of the reducible species in solution was uncertain and the reaction schemes were complex.

Hexavalent fluorides of tantalum and niobium can be prepared (59) by the electrolysis of molten FLINAK containing the quinivalent ions using an inert graphite anode. The oxidation process has been studied by chronopotentiometry. Electrodeposition of tantalum from solutions of  $K_2TaF_7$  in molten FLINAK occurs (57) in two steps: the first step  $[TaF_7]^{2-} + 3e \rightarrow TaF_2(s) + 5F^-$  is diffusion controlled and highly reversible while the second step  $TaF_2(s) + 2e \rightarrow Ta + 2F^-$  is irreversible and not diffusion controlled. This mechanism for the electroreduction of tantalum has been further supported by Inman et al. (49) from their investigations of the same system in equimolar NaF-KF at 730° C. The low value of the diffusion coefficient,  $1.5 \times 10^{-5}$  cm<sup>2</sup>/sec at 750° C, and an activation energy of 8.5 kcal/mol, are consistent with a highly coordinated species such as  $[TaF_7]^{2-}$ .

Electroreduction of Ta(V) (added as Ta<sub>2</sub>O<sub>5</sub> or NaTaO<sub>3</sub>) from its solutions in molten Na<sub>3</sub>AlF<sub>6</sub> has been studied (60) at 1000 °C by chronopotentiometry. The reduction was an apparent one step, diffusion controlled, five electron process without any chemical intermediate steps. The diffusion coefficient of Ta(V) at 1000 °C was  $(7.1 \pm 0.3) \times 10^{-5}$  cm<sup>2</sup>/sec.

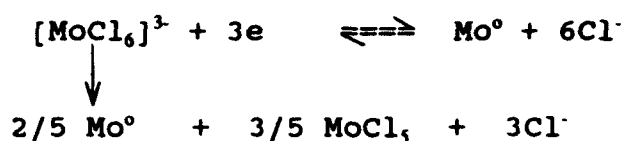
**2.7. Chromium.** Electroreduction of Cr(III) to Cr(0) in LiCl-KCl at 500° C proceeds (61) in two steps:  $Cr(III) + e \rightarrow Cr(II)$  and  $Cr(II) + 2e \rightarrow Cr(0)$ . The intermediate Cr(II) reacts with the solvent anions to form insoluble CrCl<sub>2</sub>. The kinetic parameters for the chemical and the charge transfer steps have been reported. No adsorption of any species present in solution could be detected on the vitreous carbon working electrode.

The electrode processes  $\text{Cr(II)} + 2\text{e} \rightarrow \text{Cr(0)}$  and  $\text{Cr(III)} + \text{e} \rightarrow \text{Cr(II)}$  in  $\text{LiCl-KCl}$  have been investigated (62) at  $500^\circ\text{C}$  by chronopotentiometry and steady-state voltammetry. Reduction of  $\text{Cr(II)}$  to the metal proceeded in a single, irreversible step with  $n$  values between 1.18 and 1.33. Adsorption of  $\text{Cr(II)}$  ions played a part in the electrode process; the adsorption effects increased with increasing concentration of the electroactive cations. Addition of fluoride ions to the solution did not affect the electrode process. The anodic oxidation of  $\text{Cr(II)}$  to  $\text{Cr(III)}$  was a one electron process with interference from the adsorption of  $\text{Cr(II)}$  cations. Three waves were observed in the reduction of  $\text{Cr(III)}$  to  $\text{Cr(0)}$  in  $\text{LiCl-KCl}$  at  $500^\circ\text{C}$ . The most cathodic wave corresponded to the reduction of  $\text{Cr(II)}$ . The first two waves were postulated to be due to the reduction of  $\text{Cr(III)}$  containing species which proceeded in two different steps; the first one being diffusion controlled followed by an adsorption controlled wave. The addition of fluoride ions did not show any significant effect.

Reduction of  $\text{Cr(III)}$  in  $\text{NaCl-KCl}$  on a Pt electrode at  $700$  to  $800^\circ\text{C}$  proceeded (63) in two steps as evidenced by chronopotentiometry. The first step was a diffusion controlled, reversible, one electron process followed by a two electron reduction step.

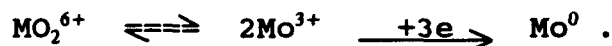
The electrochemical reduction of  $\text{Cr(VI)}$  on a Pt electrode in molten  $\text{Na}_2\text{B}_4\text{O}_7$  at  $800^\circ\text{C}$  occurred in two steps as studied (64) by linear sweep voltammetry and chronopotentiometry. The first step was a reversible, diffusion controlled, three-electron process. The diffusion coefficient of  $\text{Cr(VI)}$  at  $800^\circ\text{C}$  was  $1.9 \times 10^{-7} \text{ cm}^2/\text{sec}$ .

**2.8. Molybdenum.** Electroreduction of molybdenum (65) from  $\text{LiCl-KCl-K}_3\text{MoCl}_6$  baths at  $600^\circ\text{C}$  is irreversible (but cf. (66)). When the concentration of  $\text{K}_3\text{MoCl}_6$  was low, the plating bath was less stable and, therefore, the following reaction steps have been proposed:



The stability of the plating bath when  $\text{K}_3\text{MoCl}_6$  was present in high concentrations was due to the formation of  $[\text{Mo}_2\text{Cl}_9]^{3-}$  ions. The electroreduction of Mo(III) in LiCl-KCl at  $567^\circ \text{C}$  and NaCl-KCl (20:80 mol %) at  $765^\circ \text{C}$  has been studied by Inman and Spencer (67) in the presence and absence of added fluoride ions. It has been shown that the overall electroreduction process in both melts included a slow coupled chemical step, involving the slow dissociation of the multinuclear species  $[\text{Mo(III)}]_n$ . At the higher temperatures the value of  $n$  was shown to be 2. The addition of fluoride ions to the melts caused the overall electroreduction process to become faster (*i.e.* more reversible) which can be related to a decreasing stability of the multinuclear species.

For the study (49) of the reduction of Mo(III) in NaCl-KCl (20:80 mol %) at  $760^\circ \text{C}$ , Mo(III) was generated in the solution by *in situ* anodic dissolution. At concentrations of molybdenum  $< 2 \times 10^{-2} \text{M}$ , only one irreversible wave was observed and the overall process could be represented as



At high concentration of Mo(III), two waves were observed on the chronopotentiogram. The second wave, which occurred at more cathodic potential, was much shorter than the first wave and occurred at the same potentials as the single wave obtained at low Mo(III) concentrations. It was confirmed that the second wave was due to a molybdenum-containing species and could be explained in terms of the reduction of a dinuclear species containing molybdenum in the tripositive oxidation state. Electrodeposition of molybdenum from FLINAK proceeded (68)

irreversibly in a single, three-electron step with an average valence of 3.3. The  $\alpha_n$  value was  $2.0 \pm 0.2$  as evaluated from an approximately linear plot of  $E$  vs.  $\log (\tau^{1/2} - t^{1/2})$  at  $800^\circ \text{C}$ . The irreversibility, due to the slow dissociation of a polynuclear complex anion of molybdenum with fluoride to a mononuclear ion, was greater in the fluoride system and extended to higher temperatures, than in the molybdenum chloride system (65).

**2.9. Tungsten.** Electrochemical reduction of W(IV) and W(V) has been studied (56) in LiCl-KCl at  $450^\circ \text{C}$  by voltammetry, cyclic voltammetry and chronopotentiometry. Reduction of W(IV) occurs in two highly irreversible steps to the metal. The first step is a one electron transfer and the second a three electron reduction. Oxidation of W(IV) to W(V) proceeds in a single irreversible step. Tungsten(V) also undergoes a two step reduction to the metal; a two electron reduction followed by a three electron transfer. The electrochemical reduction of  $\text{K}_3\text{W}_2\text{Cl}_9$  solutions in LiCl-KCl at  $450^\circ \text{C}$ , as studied (69) using linear sweep voltammetry, chronopotentiometry, and coulometry, was found to be a single, three electron, diffusion controlled, irreversible process. The diffusion coefficient of the electroactive species was  $0.71 \times 10^{-5} \text{ cm}^2/\text{sec}$ . The reduction product was found to be tungsten metal from its X-ray diffraction powder pattern.

The electrodeposition of tungsten from FLINAK at  $600^\circ \text{C}$  from solutions prepared by reacting  $\text{WF}_6$  with W in the melt occurs (68) irreversibly in a single, four-electron step, with an average valence of 4.48. The irreversibility was due to the slow dissociation of a polynuclear complex anion of tungsten with fluoride to a mononuclear ion.

### **3. THE ACTINIDES**

Chronopotentiometry has been applied extensively to investigate the electrochemical oxidation/reduction of various actinides in molten salt solutions as described below.

**3.1. Thorium.** Thorium (IV) is reduced reversibly to the metal with alloy formation between deposited thorium and the nickel electrode in molten FLINAK at 500 °C as studied (70) by voltammetry at nickel and tungsten electrodes. Temperature dependence of Th (IV) diffusion coefficients was Arrhenian in chloride and chloride-fluoride melts of sodium and potassium in the temperature range 680-830° C as determined (71) by chronopotentiometry. A molybdenum indicator electrode was used in chloride melts while a zinc-plated molybdenum electrode was employed in the chloride-fluoride melt. Diffusion coefficients of Th(IV) were less in the fluoride-containing melt than in the chloride melt due to the strengthening of the bond between thorium and fluoride ions and the consequent decrease in their mobility. The Stokes-Einstein equation was not applicable.

**3.2. Uranium.** The electrochemistry of uranium in chloride melts has been studied by many techniques; only the chronopotentiometric work is given here. The equilibrium potentials of the couples U (III)/U(0) and Pu(III)/Pu(0) in LiCl-KCl have been determined (72) using chronopotentiometry. The technique worked satisfactorily, except at low temperatures, irrespective of whether the reduced form of the metal on a W microelectrode was solid or liquid. The rate determining step (73-75) for the reduction  $U(IV) + e \rightleftharpoons U(III)$  in LiCl-KCl was not the electron transfer, but the rearrangement of the structure of the reduced chlorocomplexed uranium ions which followed the electron transfer. Caligara et al. (73-75) discussed the diffusion mechanism and put forward a hypothesis that for each ion there is a temperature at which the diffusion takes place according to the viscous flow mechanism. Diffusion coefficients of U(IV) and U(III) were evaluated as a function of temperature. Concentrations of U(IV) and U(III) may be determined (76) when present together in the same solution. Leseur (77) studied the electrochemical behavior of U(IV) and Pu(III) in molten LiCl-KCl and determined the diffusion coefficients of U(III) and U(IV) in the



presence of F<sup>-</sup> and Pu(III) ions. Thalmayer et al. (78) also evaluated the diffusion coefficients of U(IV).

Diffusion coefficients of U(III) and U(IV) in molten LiCl-CsCl in the temperature range 400-600 °C and also in RbCl-CsCl melt in the temperature region 670-900 °C have been determined (79). The values of the diffusion coefficients in the latter melt are improbably high.

Temperature dependence (80) of diffusion coefficients of U(III) and U(IV) in NaCl-KCl in the range 680-900° C was Arrhenian. The Stokes-Einstein equation was not applicable.

The electrochemical reduction (81) of U(IV) in NaCl-AlCl<sub>3</sub> (50-50 and 38.2-61.8 mol %) melts was not perfectly reversible, but the reversibility increased with temperature. Similar results have been obtained in LiCl-KCl. However, there is a major difference in the reduction mechanism in different melts. In NaCl-AlCl<sub>3</sub>, for the reduction of U(IV), the electron transfer is the rate controlling step. In contrast, for the reduction of U(IV), Np(IV) and Pu(IV) in LiCl-KCl, the rate determining step is not the electron transfer itself but the rearrangement of the chlorocomplex following the electron transfer. The diffusion coefficients of U(IV) and activation energies for diffusion in the temperature range 250-400° C have been evaluated (81) for both NaCl-AlCl<sub>3</sub> melts. Values of the electrochemical transfer coefficient and activation energy for the charge transfer process have also been calculated (81).

The electrochemical reduction and oxidation of U(IV) in molten FLINAK at 500° C have been investigated (70). At a Pt microelectrode, U(IV) underwent a two-step reduction. The first step was the reduction of U(IV) to U(III) and was complicated by the disproportionation of U(III) to regenerate U(IV). The second step involved the formation of uranium metal from U(III). A voltammetric study revealed that U(IV) was oxidized both at platinum and graphite electrodes in FLINAK according to a mechanism based on the disproportionation of the electrochemically generated U(V). Similar disproportionation of U(V) was also reported by Manning and Mamantov (82) in molten LiF-

BeF<sub>2</sub>-ZrF<sub>4</sub>. Again in the LiF- BeF<sub>2</sub>-ZrF<sub>4</sub> melt, Mamantov and Manning (83, 84) studied the electrochemical reduction of U(IV) over the temperature range 480-620° C on Pt, Mo, W, Ta, Pt-Rh (10 %), and graphite working electrodes. Weak adsorption of U(IV) occurred at the Pt and Pt-Rh electrodes, with simultaneous electrolysis of diffusing and adsorbed species. Disproportionation of the electrochemically generated U(V) to U(IV) and U(VI) was observed (82) during the electrochemical oxidation of U(IV) in molten LiF-BeF<sub>2</sub>-ZrF<sub>4</sub> at 500° C at unsheathed pyrolytic graphite and Pt-Rh electrodes.

The electrochemical reduction of U(VI) to U(V) on a Pt electrode in molten Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> at 800 °C was a reversible, diffusion controlled process as studied (64) by linear sweep voltammetry and chronopotentiometry. The diffusion coefficient of the U(VI) species at 800 °C was  $4 \times 10^{-7}$  cm<sup>2</sup>/sec , the activation energy of diffusion being 34.8 kcal/mol.

Chronopotentiometry was also employed (45) to study the reduction of UO<sub>2</sub><sup>2+</sup> and the oxidation of U(IV) in molten equimolar NaPO<sub>3</sub>-KPO<sub>3</sub>. At 700° C, the diffusion coefficients of UO<sub>2</sub><sup>2+</sup> and U(IV) are  $1.26 \times 10^{-7}$  and  $0.318 \times 10^{-7}$  cm<sup>2</sup>/sec in this highly viscous melt. Uranyl ion yielded a two-electron reduction wave. The large transition times (of the order of 2-16 sec), reversibility of the electrode processes, and diffusion coefficients have been criticized (85). However, Wolfe and Caton (86) claim that in such viscous melts long transition times are permissible.

The chronopotentiograms for the reduction of UO<sub>2</sub><sup>2+</sup> in LiCl-KCl were reported (76, 87) to be similar to those obtained by Stromatt (88) in NaCl-KCl. The value of the ratio  $\tau_2/\tau_1 = 3$  where  $\tau_1$  and  $\tau_2$  are the transition times for the reactions  $\text{UO}_2^{2+} + e \rightarrow \text{UO}_2^+$  and  $\text{UO}_2^+ + e \rightarrow \text{UO}_2(\text{s})$ . Diffusion coefficients of UO<sub>2</sub><sup>2+</sup> in LiCl-KCl in the presence of F<sup>-</sup> and of Pu(III) ions have also been determined (77).

Electroreduction of UO<sub>2</sub><sup>2+</sup> on a platinum microelectrode in NaCl-KCl proceeds (88) in two steps:



These observations have been verified by measurements of the pseudo-capacity of the polarized cathode as a function of its potential. The heterogeneous rate constant for the reduction of  $\text{UO}_2^{2+}$  to  $\text{UO}_2^+$  is quite large ( $2 \times 10^{-2}$  cm/sec). The chronopotentiometric reduction of  $\text{UO}_2^{2+}$  in NaCl-KCl has been investigated (80) and its diffusion coefficients have been determined at various temperatures.

The electroreduction of  $\text{UO}_2^{2+}$  in molten KCNS as studied (89) by chronopotentiometry and polarography was diffusion controlled and proceeded in two steps:  $\text{UO}_2^{2+} + e \rightleftharpoons \text{UO}_2^+$ ;  $\text{UO}_2^+ + e = \text{UO}_2(\text{s})$ . At 185° C the diffusion coefficient of  $\text{UO}_2^{2+}$  was  $6.56 \times 10^{-7}$  cm<sup>2</sup>/ sec which is about one-third of that for  $\text{Pb}^{2+}$  in the same melt (90) at the same temperature.

**3.3. Neptunium.** The electroreduction  $\text{Np(IV)} + e \text{ ---> } \text{Np(III)}$  in LiCl-KCl has been studied (91) and the diffusion coefficients of Np(IV) have been evaluated in the temperature region 400-500° C. The electrochemical reduction of Np(IV) was followed (91) by a slow rearrangement of the shell of complexing chloride ions. The activation energy for diffusion decreased with increasing temperature, while the reversibility of the electrode reaction increased. Martinot and Duyckaerts (92) carried out a chronopotentiometric study of the kinetics of the oxidation reaction  $\text{Np(III)} \text{ ---> } \text{Np(IV)} + e$  in LiCl-KCl and evaluated the diffusion coefficient of Np(III) in the temperature interval 400-650° C. For the oxidation of Np(III) also, the slow step was the rearrangement of the chlorocomplex after the electron transfer. In the temperature range 400-550° C, Np(IV) in LiCl-KCl may be determined quantitatively (76) with an accuracy of  $\pm 4\%$  using chronopotentiometry.

Chronopotentiometry has been employed (93) for identifying  $\text{NpO}_2^{2+}$  in LiCl-KCl. A chronopotentiometric study of the reactions  $\text{NpO}_2^{2+} + 2e \text{ ---> } \text{NpO}_2(\text{s})$  and  $\text{NpO}_2^+ + e \text{ ---> } \text{NpO}_2(\text{s})$  in LiCl-KCl has been reported (94). The diffusion coefficients of the oxygenated

neptunium ions,  $\text{NpO}_2^{2+}$  and  $\text{NpO}_2^+$  were measured up to  $400^\circ \text{C}$ , but disproportionation of  $\text{NpO}_2^+$  to  $\text{NpO}_2(\text{s})$  occurred at higher temperatures.

The electrochemical behavior of  $\text{NpO}_5^{3-}$  in molten  $\text{KOH-NaOH}$  has been investigated (95). At  $240^\circ \text{C}$ , the reduction proceeded in a single step:  $\text{NpO}_5^{3-} + 3\text{e} \rightarrow \text{NpO}_2 + 3\text{O}^{2-}$  while at  $290^\circ \text{C}$  the reduction took place in two steps:  $\text{NpO}_5^{3-} + 2\text{e} \rightarrow \text{NpO}_2^+ + 3\text{O}^{2-}$  followed by  $\text{NpO}_2^+ + \text{e} \rightarrow \text{NpO}_2$ . The diffusion coefficients of  $\text{NpO}_5^{3-}$  were determined.

**3.4. Plutonium.** Chronopotentiometry has been used to study (96) the reduction of  $\text{Pu(III)}$  in  $\text{LiCl-KCl}$  at a tungsten electrode. At  $400^\circ \text{C}$   $\text{Pu(III)}$ , possibly in the form of a complex ion, undergoes a direct three-electron reduction to the metal. At temperatures above  $400^\circ \text{C}$ , an equilibrium apparently exists between two complex species of plutonium and the rate of transformation from one form to another, which preceded the electron transfer itself, was the rate determining step. These results, which indicate that the behavior of  $\text{Pu(III)}$  differed from that of  $\text{U(III)}$  (74) and  $\text{Np(III)}$  (92) when the temperature exceeded  $400^\circ \text{C}$ , have been questioned by Kertes (10). Martinot and Duyckaerts (97), on the other hand, have investigated the oxidation of  $\text{Pu(III)}$  to  $\text{Pu(IV)}$  in  $\text{LiCl-KCl}$  and reported diffusion coefficients of  $\text{Pu(III)}$  over a similar range of temperature. The values of the diffusion coefficients of  $\text{Pu(III)}$  obtained by the two independent studies (96, 97) are in remarkably good agreement. The electroreduction of  $\text{Pu(IV)}$  in  $\text{LiCl-KCl}$  has also been studied (98). The diffusion coefficients of  $\text{Pu(IV)}$ ,  $\text{Np(IV)}$  and  $\text{U(IV)}$  have been evaluated (98) in the temperature range  $400$  to  $650^\circ \text{C}$  and the temperature dependence of the activation energy for diffusion has been discussed on the basis of the hole theory for molten salts. Leseur (77) has also studied the electrochemical behavior of  $\text{Pu(III)}$  in  $\text{LiCl-KCl}$ .

The electrochemical reduction of  $\text{PuO}_5^{3-}$  has been studied (99) in molten  $\text{NaOH-KOH}$  at  $240^\circ \text{C}$ . The reduction proceeded in two steps:  $\text{PuO}_5^{3-} + \text{e} \rightarrow \text{PuO}_2^{2+} + 3\text{O}^{2-}$ ;  $\text{PuO}_2^{2+} + 2\text{e} \rightarrow \text{PuO}_2$ , the

latter step being rate controlling. It was concluded that  $\text{PuO}_3^3$  is less stable than  $\text{NpO}_3^3$  in molten  $\text{NaOH-KOH}$  at  $240^\circ \text{C}$ . On spontaneous reduction,  $\text{PuO}_3^3$  gave only  $\text{PuO}_2^{2+}$ .

**3.5. Americium.** The reduction (100) of  $\text{Am(III)}$  on a Pt electrode in  $\text{LiCl-KCl}$  was a single, three-electron, diffusion controlled process which was not reversible. The diffusion coefficients of  $\text{Am(III)}$  have been evaluated in the temperature interval  $400-650^\circ \text{C}$ . The diffusion mechanism has been discussed on the basis of the hole theory for molten salts. It was not possible to oxidize  $\text{Am(III)}$  on a Pt or carbon electrode.

The electrochemical behavior of americium(VI) species in  $\text{NaOH-KOH}$  melt has also been investigated (101). The  $\text{AmO}_2$  became soluble in the melt only when oxygen was bubbled through it. The  $\text{Am(VI)}$  species could not be definitely defined; it probably exists as  $\text{AmO}_2^{2+}$  or  $\text{AmO}_4^{2-}$  in the melt. Like  $\text{UO}_2^{2+}$ , the reduction of americium(VI) containing species proceeded in two steps. The nature of both these processes was not very well understood. Assuming the first reduction to be a single electron process, the diffusion coefficient of the electroactive species was calculated to be  $(0.65 \pm 0.2) \times 10^{-5} \text{ cm}^2/\text{sec}$  at  $250^\circ \text{C}$ .

**3.6. Curium.** The electrochemical reduction (102) of  $\text{Cm(III)}$  on a platinum electrode in  $\text{LiCl-KCl}$  was a three-electron, diffusion controlled process. The diffusion coefficients of  $\text{Cm(III)}$  have been evaluated in the temperature range  $400-550^\circ \text{C}$ . The activation energy for diffusion was found to be constant in the above temperature range, in contrast to the behaviour of other actinide  $3+$  ions (U, Np, Pu, Am). However, the present author (103) could fit the data of Martinot et al. (102) into the Arrhenius equation with standard deviations of 5.6 % for  $\text{U(III)}$ , 2.7 % for  $\text{Np(III)}$ , 2.1 % for  $\text{Pu(III)}$ , and  $\text{Pu(IV)}$ , respectively implying that the energy of activation is independent of temperature for the diffusion of these ions.

#### 4. THE OXYANIONS

Chronopotentiometry, along with other electroanalytical techniques, have been widely used to understand the electrochemical behavior of various oxygen-containing anions in solutions of different molten salt systems as discussed below.

**4.1. Nitrite.** Diffusion coefficients of nitrite ions in molten  $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$  have been determined (104). Electrochemical behavior of  $\text{NO}_2^-$  ion dissolved in molten  $\text{NaNO}_3\text{-KNO}_3$  has been studied (105) in the temperature range 275-350° C using voltammetry and anodic chronopotentiometry. At 300 °C, the oxidation of  $\text{NO}_2^-$  was a reversible, one electron process represented by the reaction  $\text{NO}_2^- \rightleftharpoons \text{NO}_2(\text{g}) + \text{e}$ . These results are in agreement with the voltammetric study of Swofford & McCormick (106). When the current was reversed before the transition time, ratios of forward to reverse transition times were always greater than the theoretical value of 3. This may be due to the fact that a part of the product of the forward step ( $\text{NO}_2$ ) is lost by volatilization and/or reaction. When the solution was acidified, the nitrite wave was decreased or disappeared. No new wave appeared which could be attributed to the nitrosonium,  $\text{NO}^+$ , ion. The nitronium ion,  $\text{NO}_2^+$ , could not be detected in the melt under study. Anodic chronopotentiometry of nitrite ions has been studied (107) at oxidized platinum electrodes in  $\text{NaNO}_3\text{-KNO}_3$ . Reproducible potential-time curves were obtained only when the platinum anode was biased sufficiently positive to maintain an oxide film. Dissociation of nitrite ions proceeds according to the reaction:  $\text{NO}_3^- \rightarrow \text{NO}_2^- + 1/2 \text{O}_2$  rather than  $\text{NO}_3^- \rightarrow \text{NO}_2^+ + \text{O}^{2-}$  (cf. 108);  $\text{NO}_2^+$  ion, if it exists, could only be a short lived intermediate at the anode surface. The electrochemical behavior of nitrite ions has been investigated (109) in  $\text{NaNO}_3\text{-KNO}_3$  at 250° C. These results supported the postulate that a reversible couple is formed between nitrite ions and  $\text{NO}_2$  gas in the melt. Ingram and Lewis (110) have investigated the behavior of  $\text{NO}_2^-$  oxidation in molten  $\text{KNO}_3\text{-Ca(NO}_3)_2$  (62-38 mol %). It seemed probable that the acid-base reaction between  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  ions

favored decomposition reactions of the type  $\text{NO}_2^- + \text{NO}_3^- \longrightarrow 2\text{NO}_2 + \text{O}^{2-}$ .

**4.2. Nitrate.** Reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  and  $\text{O}^{2-}$  on Pt microelectrodes has been investigated (111, 112) in  $\text{NaNO}_3\text{-KNO}_3$  at  $250^\circ\text{C}$ . The results of this study confirmed the existence of a surface process of  $\text{Na}_2\text{O}$  formation, established by a polarographic technique.

**4.3. Hydroxide.** Topol et al. (105) observed an anodic wave for the solutions of hydroxide in molten  $\text{NaNO}_3\text{-KNO}_3$  at  $-0.3\text{V}$ , as did El Hosary and Shams El Din (113). A well defined wave which obeyed the Sand equation was obtained (110) for  $\text{OH}^-$  oxidation in molten  $\text{KNO}_3\text{-Ca(NO}_3)_2$  (62-38 mol %). The overall stoichiometry of the electrode reaction could be represented as  $2\text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ .

**4.4. Oxalate.** Electrochemical behavior of oxalate ions in molten  $\text{NaNO}_3\text{-KNO}_3$  has been studied (109) at  $250^\circ\text{C}$ . Oxalate was found to remain essentially undissociated until catalytically decomposed to yield oxide.

**4.5. Oxide.** Electrochemical oxidation (109) of oxide ions in  $\text{NaNO}_3\text{-KNO}_3$  melt at  $250^\circ\text{C}$  proceeds by a one-electron process, and the product, peroxide, is decomposed in a subsequent chemical step. The behavior of electrogenerated oxide ions in  $\text{NaNO}_3\text{-KNO}_3$  has been investigated (113) in the temperature region  $240\text{-}350^\circ\text{C}$ . The anodic wave exhibited two diffusion controlled steps corresponding to the reactions  $\text{O}^{2-} \longrightarrow \frac{1}{2}\text{O}_2 + 2\text{e}$  and  $\text{NO}_2^{2-} \longrightarrow \text{NO}_2 + \text{e}$ .

Electrochemical oxidation of oxide ions on gold electrodes has been examined (114) in  $\text{LiF-BeF}_2\text{-ZrF}_4$  (65.6-29.4-5.0 mol %) and  $\text{LiF-BeF}_2\text{-ThF}_4$  (72-16-12 mol %) melts in the temperature interval  $500\text{-}710^\circ\text{C}$  by chronopotentiometry and cyclic voltammetry. On electro-oxidation, oxide ions gave atomic oxygen which rapidly recombined to generate chemisorbed  $\text{O}_2$  or reacted with

oxide ions to form peroxide ions which were further oxidized. The addition of sodium peroxide to the melt did not give any additional wave. The behaviour of superoxide,  $O_2^{\cdot -}$ , ion was the same as that of peroxide indicating that the superoxide was unstable and decomposed to peroxide and other products immediately after coming into contact with the melts.

**4.6. Peroxide.** An inflection on the cathodic voltammograms and chronopotentiograms for the solution of  $Na_2O_2$  (contaminated with hyperoxide) in LiCl-KCl at  $585^\circ C$  has been assigned (115) to the reduction of hyperoxide,  $O_2^-$  ions. The behavior of  $O_2^{2-}$  in  $NaNO_3$ - $KNO_3$  has been studied (113) in the temperature range  $240$ - $350^\circ C$ . Two, approximately equal, anodic waves have been obtained (105) for the oxidation of  $Na_2O_2$  in  $NaNO_3$ - $KNO_3$ . The first wave, probably due to  $O_2^{2-}$ , was observed at  $-0.2 V$  and the second involving  $O_2^{\cdot -}$  at  $+0.3 V$ . However, only a single wave was reported by Swofford and McCormick (106) in their voltammetric studies.

The electrochemical behaviour of peroxide and superoxide,  $O_2^-$  ions in  $LiF$ - $BeF_2$ - $ZrF_4$  (65.6-29.4-5.0 mol %) and  $LiF$ - $BeF_2$ - $ThF_4$  (72-16-12 mol %) melts has been examined (114) using chronopotentiometry and cyclic voltammetry. The behaviour of  $O_2^-$  ions was the same as that of peroxide due to its decomposition into peroxide and other products immediately after addition into the melts.

**4.7. Carbonate.** Electroreduction of  $CO_3^{2-}$  anion in NaCl-KCl has been studied (116, 117) at  $700^\circ C$  using oscillopolarographic and chronopotentiometric techniques. The potential for direct discharge of  $CO_3^{2-}$  anion was not reached since deposition of the alkali metal started. The carbonate is first converted into  $CO_2$  through the acid-base reaction  $CO_3^{2-} \rightleftharpoons CO_2 + O^{2-}$  which is a kinetic reaction preceding the discharge of  $CO_2$  which proceeds in two steps and could be described by the following approximate mechanism :





The initial decomposition of  $\text{CO}_3^{2-}$  to  $\text{CO}_2$  and  $\text{O}^{2-}$  has been further confirmed by chronopotentiometric studies (118) in the same melt. At  $700^\circ \text{C}$ ,  $\alpha_n$  was 0.46 and the rate constant for the electrode reaction was  $(6.69 \pm 0.52) \times 10^{-3} \text{ cm/sec}$ .

A solution of  $\text{Na}_2\text{CO}_3$  in  $\text{NaNO}_3\text{-KNO}_3$  gave rise (105) to an anodic wave.

**4.8. Sulfur-Containing Anions.** Preliminary studies of the solutions of  $\text{S}_2\text{O}_7^{2-}$  and  $\text{HSO}_4^-$  in  $\text{NaNO}_3\text{-KNO}_3$  have been carried (105) out by chronopotentiometry and voltammetry.

Woodhall (119) reported that  $\text{SO}_4^{2-}$  could be directly reduced at a cathode in  $\text{LiCl-KCl}$ . However, according to Burrows (120) and Wrench and Inman (121), the sulfate ion could not be cathodically reduced in  $\text{LiCl-KCl}$  which had been purified by pre-electrolysis under vacuum. The reduction waves for  $\text{SO}_4^{2-}$  observed by Woodhall (119) are probably due to the catalytic effect of traces of water or hydroxide and the possible mechanism for the reduction of  $\text{SO}_4^{2-}$  under these conditions could be:  $\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + \text{O}^{2-}$ ;  $\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$ . The chronopotentiometric investigations of Wrench and Inman (121) also indicated that sulfate ion is not directly reduced to lower valent sulfur compounds in  $\text{NaCl-KCl}$ , in agreement with the voltammetric work of Bukun and Ukshe (122). The cathodic chronopotentiometric waves observed (121) upon the addition of sodium metaphosphate to a solution of sodium sulfate in  $\text{NaCl-KCl}$  are due to the reduction of free or complexed sulfur trioxide (e.g.  $\text{S}_2\text{O}_7^{2-}$ ) formed by the acid-base reaction between the metaphosphate and sulfate ions:  $2\text{PO}_3^- + \text{SO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{SO}_3$ . In the presence of oxide ions (added as lithium oxide) the transitions were better defined. The plots of cathode potential vs.  $\log (\tau^{1/2} - t^{1/2})/t^{1/2}$  indicated that the overall electrode process was diffusion controlled, involved soluble reactants and products, and transfer of a single electron. The electrode reaction  $\text{SO}_3 + e \rightarrow \text{SO}_3^-$  followed by the chemical combination reaction  $\text{SO}_3^- + \text{SO}_3^- \rightarrow \text{S}_2\text{O}_6^{2-}$  was postulated. No cathodic chronopotentiograms were observed upon the addition of pyrophosphate ions to the melts

containing sulfate ions.

**4.9. Phosphates.** Chronopotentiometry has also been employed to study the electroreduction of solutions of various phosphates in molten halides and the products arising from the electrolysis of molten phosphates. Laitinen and Lucas (123) investigated the electrochemical reduction of trimetaphosphate in LiCl-KCl on platinum, gold and pyrolytic graphite electrodes over the temperature interval 450-700° C. At 450° C, two reduction waves were observed. Current reversal chronopotentiometry demonstrated that a very fast chemical reaction followed electron transfer of the first reduction step. The chronopotentiometry of glassy sodium metaphosphate has also been reported; two reduction waves were observed with quarter-wave potentials identical to those observed with trimetaphosphate. The reduction product of trimetaphosphate was found to be pyrophosphate. Typical chronopotentiograms for  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$ ,  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_3\text{P}_3\text{O}_9$  have been depicted at 450° C. The influence of temperature upon the shape of the potential-time curves and the number of reduction steps has been investigated in the range 450-700° C. The reduction process was found to be very complex even at the highest temperature because of prior chemical reactions. A reduction scheme, consistent with the experimental observations, has been proposed.

Solutions of a number of phosphates in NaCl-KCl have been examined (124, 125) using chronopotentiometry. Sodium orthophosphate showed a reversible two-electron reduction step involving soluble reactants and products. This corresponded to the reduction of pentavalent phosphorus to the trivalent state; the overall product probably results from further chemical reactions. The potential-time curves for the electrolysis of sodium pyrophosphate solutions in NaCl-KCl at 670° C showed two transitions; the first was due to the reduction of the orthophosphate ion and the second corresponded to the reduction of pyrophosphate ion. Above 750° C the second transition had disappeared due to the complete conversion of pyrophosphate into

orthophosphate at this temperature. The electrolysis of sodium tripolyphosphate solutions in NaCl-KCl at 750° C exhibited three reduction steps corresponding to ortho, pyro and tripolyphosphate ions.

The electroreduction of molten sodium metaphosphate using a tungsten wire microelectrode was investigated (124, 125) by chronopotentiometry and other techniques. In the highly polymerized sodium metaphosphate melt, only the lower polymer phosphate ions get reduced at the cathode. Chronopotentiometry indicated that a chemical reaction, probably depolymerization, precedes the reduction process. The extent of depolymerization increased with temperature and the availability of lower polymers was affected by the current density. At low current densities there was sufficient time for the prior depolymerization to occur and only the decomposition of the orthophosphate was observed giving phosphorus evolution. At high current densities there was not sufficient time for complete depolymerization and polymers higher than the monomer could be reduced.

**4.10. Silicate.** Solutions of sodium silicate in NaCl-KCl have been studied (126) in the temperature range 660-800° C. The presence of ortho-, pyro- and trisilicate ions has been identified by means of chronopotentiometry. At 660° C, three reduction steps were observed on the chronopotentiogram. The first two processes correspond to the reduction of the ortho- and pyrosilicate oxyanions,  $\text{SiO}_4^{4-}$  and  $\text{Si}_2\text{O}_7^{6-}$ , respectively. The third transition was reduced with increasing temperature and only the first two transitions were left at 780° C. The first step was a reversible, two-electron process, probably  $\text{SiO}_4^{4-} + 2e \rightarrow \text{SiO}_2^{2-} + 2\text{O}^{2-}$ , followed by the decomposition  $2\text{SiO}_2^{2-} \rightarrow \text{SiO}_4^{4-} + \text{Si}$ . In the electroreduction of the pyrosilicate anion, the oxidation state of silicon is reduced from four to two.

**4.11. Chromium-Containing Oxyanions.** Electrochemical reduction of chromate in molten salts has been investigated by various workers using different electroanalytical techniques. Black and

DeVries (127) found two voltammetric waves for chromate in LiCl-KCl at 408° C using platinum microelectrodes and concluded that the two waves correspond to successive reductions of Cr(VI) to Cr(III) and Cr(II), respectively. On the other hand Ferguson (128) and Bhatia (129) observed that the reduction proceeded in a single, three electron step at 450° C. Chronopotentiometric studies (130) revealed a single, irreversible, diffusion controlled, three-electron step for the reduction of chromate in LiCl-KCl. Current reversal chronopotentiometry showed abnormally short reverse transition times, which decreased markedly with increasing temperature but increased somewhat in the presence of added oxide ion. If the current density for electrolysis was higher than a particular limit (a few mA/cm<sup>2</sup>), the major product of the electrode process was the insoluble compound Li<sub>5</sub>CrO<sub>4</sub>. However, if the quantity of electricity used was less than that required for the formation of the insoluble deposit, the primary reduction product was the ion CrO<sub>4</sub><sup>5-</sup>, which further decomposes:



Laitinen and his coworkers (130-135) have examined extensively the effect of the addition of a variety of divalent metal ions M(II), where M = Mg, Ca, Zn, Ni, or Co, on the reduction mechanism of chromate in LiCl-KCl. These investigations have been reviewed (133). The effect of the addition of these divalent metal ions was to shift the reduction potential of chromate in the anodic direction by 0.4 to 1.0 V depending on the ion M(II) and to alter the chemical part of the above mechanism to yield a non-stoichiometric compound having the empirical formula Li<sub>x</sub>M<sub>y</sub>CrO<sub>4</sub>, where x + 2y = 5. This type of compound has been observed for Mg(II), Ni(II) and Zn(II). The exact composition of the product depends on the conditions of electrolysis, specifically the current density, the temperature, and the molar ratio M(II)/Cr(VI). The number of Faradays required per mole of product is always three as in the above sequence. The mole fractions of lithium in the compound vary

from 0.25 to 0.5 for Mg(II) and from 0.6 to 0.8 for Ni(II), while the Zn(II) compound is always stoichiometric with  $x$  equal to 1.0. The mole fraction of lithium in the compound increases with increase in temperature and decreases when the current density or the concentration of M(II) is increased. However, the product obtained with Zn(II) is unaltered by changes in the preparative conditions (132). These compounds are very thermally stable and resistive to oxidation. Only the Zn(II) product can be partially reoxidised electrochemically.

The effect of the addition of Co(II) was different (131, 132) from that observed for other divalent metal ions. A compound having the general formula  $\text{Li}_x\text{Co}_y\text{CrO}_4$  could be obtained under certain experimental conditions, but the relation  $x + 2y = 5$  did not hold. The mole fraction of lithium in the compound increased as the current density or Co(II)/Cr (VI) molar ratio in the solution increased. The value of  $x$  decreased as the cathode potential became more anodic or as the temperature of the melt increased. The number of Faradays required per mole of the product depends on the stoichiometry, and hence on the experimental conditions, and is described by the relationship  $n = 2 + x$ . At low cathode potential, low Co(II)/Cr(VI) mole ratio, high temperature, and high Co(II) concentration a limiting product  $\text{Co}_2\text{CrO}_4$  is obtained for which  $n = 2$ . When this is the product, the reduction potential of chromate is anodically shifted by 0.62 V.

However, it has been recently shown (136) that the addition of dehydrated Ca(II) ions to LiCl-KCl has no effect on the reduction of chromate. The positive shift in the reduction potential of chromate, reported earlier (130), was due to the traces of water associated with hygroscopic  $\text{CaCl}_2$ . Presence of water in the system has quite a remarkable effect on chromate reduction (*vide supra*). Addition of Mg(II), Zn(II) or Ni(II) does not affect the value of the diffusion coefficient of chromate ion, which is  $1.0 \times 10^{-5} \text{ cm}^2/\text{sec}$  at  $450^\circ \text{C}$ . However, when  $\text{Co}_2\text{CrO}_4$  is the only reduction product, the diffusion coefficient has been estimated to be  $2.0 \times 10^{-5} \text{ cm}^2/\text{sec}$  (131). An

electrochemical-chemical reaction scheme has been proposed (133) for the reduction of chromate in the presence of these divalent metal ions which accounts for the stoichiometry of the reduction products, shifts in reduction potentials and other experimental observations.

The effect of presence of moisture on the electrochemical reduction of chromate in LiCl-KCl has been investigated (136) by chronopotentiometry and coulometry. Only one wave was observed at -1.18 V vs. Pt(II), 1M/Pt reference under highly dehydrated conditions and addition of Ca(II) ions had no effect. However, in the presence of moisture two reduction waves at -0.6V and -1.18V were observed. The first reduction was found to be controlled by H<sub>2</sub>O diffusion and two water molecules and three electrons were consumed per chromate ion. The reduction mechanism has been proposed and discussed.

Reduction of chromate ion has been examined (137) in an acidic equimolar ZnCl<sub>2</sub>-KCl melt at 300° C to further characterize the Cr(IV) species proposed by Hanck and Laitinen (132) in LiCl-KCl in the presence of Zn(II). The reduction proceeds in a single, irreversible, diffusion controlled step yielding an insoluble electrode deposit which is resistant to electrochemical oxidation. The reduction product is an unstoichiometric compound of the general formula K<sub>x</sub>Zn<sub>y</sub>CrO<sub>z</sub>. The values of x, y and z depend upon the current density applied during the electrolysis. The Cr(IV) species is found to be more stable in the acidic ZnCl<sub>2</sub>-KCl melt than in neutral LiCl-KCl containing Zn (II).

Electrochemical reduction of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and CrO<sub>2</sub>Cl<sub>2</sub>, in the presence of MgCl<sub>2</sub>, in LiCl-KCl has been investigated (135) with a view to study the effect of the lower oxygen-to-chromium ratio on the composition of the electrode deposit. However, many difficulties came into the way of these studies, as the chemical attack of the cathode caused a mixture of compounds to be deposited on the electrode surface. Also, oxide ion was released to the bulk melt altering the oxygen to chromium ratio of the Cr(VI) species being transported to the electrode surface.

**4.12. Tungstate.** The electroreduction of tungstate ion in LiCl-KCl at 450 °C is found (56) to be a complex process which produces a dark insoluble compound of the form  $M_xWO_4$  ( $x > 2$ ) and tungsten trioxide. Johnston (69) also reported the reduction mechanism of tungstate ion in LiCl-KCl to be quite complicated. Voltammetry, cyclic voltammetry and chronopotentiometry suggested (69) two reduction steps. The first one was due to a solute species of low concentration and the main solute species was responsible for the more cathodic step. No definite conclusions could be drawn about the composition of the electrode deposits. Reduction of tungstate ions at a Pt electrode has also been examined (116) in NaCl-KCl at 700 °C using chronopotentiometry and linear sweep voltammetry.

**4.13. Vanadium-Containing Anions.** Electrochemical reduction of lithium metavanadate in LiCl-KCl has been investigated (138) at 450° C using chronopotentiometry, controlled potential electrolysis, chronopotentiometry with current reversal, and cyclic sweep voltammetry. Reduction of  $LiVO_3$  proceeded in two steps. The first step produced an insoluble product which underwent a chemical reaction with  $LiVO_3$  to form insoluble  $LiV_2O_5$  and  $Li_3VO_4$ . The second step produced insoluble  $LiVO_2$  and  $Li_3VO_4$ . The  $LiVO_2$  further reacted with  $LiVO_3$  to give a mixture of solid compounds one of which was  $LiV_2O_4$ . The  $VO_2$  was found to react with  $LiVO_3$  to produce  $LiV_2O_5$ . Addition of oxide ion resulted in disproportionation of insoluble  $VO_2$  in the melt to produce  $Li_3VO_4$  and  $V_2O_3$  or  $Li_3VO_4$  and  $LiVO_2$ , depending on the concentration of oxide ion.

**4.14. Molybdenum-Containing Anions.** Electroreduction of Mo(VI) compounds in LiCl-KCl has been studied (139). At 450° C,  $MoO_3$  reacts with the melt to form  $MoO_2Cl_2$ , which is probably present as the anion  $MoO_2Cl_4^{2-}$ , and pyromolybdate,  $Mo_2O_7^{2-}$ . Electrochemical reduction of both of these species yields  $MoO_2$ , which can be reoxidized to  $MoO_2Cl_2$  by current reversal. A second reduction step is also observed which can be attributed to the reduction of  $MoO_4^{2-}$  which is formed as a secondary reaction

product during the first step. The reduction of molybdate proceeded in two steps. For the first step the transition time was abnormally short which can be attributed to a slow equilibrium. The second step corresponded to a diffusion controlled reduction with  $n = 0.5$  yielding  $\text{Li}_2\text{Mo}_2\text{O}_7$  as the product.

Effect of the addition of  $\text{ZnCl}_2$  on the electrochemical reduction of molybdate in  $\text{LiCl-KCl}$  has also been examined (140). Under certain conditions, the reduction of molybdate proceeded in a diffusion controlled, single step. The addition of  $\text{ZnCl}_2$  to the system resulted in two waves corresponding to the respective reductions of  $\text{Zn(II)}$  and molybdate. An increase in the concentration of molybdate in the solution decreased the first and increased the second transition time. The equilibrium  $\text{Zn}^{2+} + \text{MoO}_4^{2-} \rightleftharpoons \text{ZnMoO}_4$  reaction has been proposed on the basis of the experimental results.

## **5. SUMMARY AND CONCLUSIONS**

The available studies on the applications of chronopotentiometry to investigate the electrochemistry of refractory metals, actinides, and oxyanions, the three areas of technological as well as academic importance, have been reviewed here. Chronopotentiometry appears to be a very versatile technique to examine the electrode processes during electrochemical reduction/oxidation of various solutes in molten salt solutions. An understanding of the reaction mechanism should help in optimization of the experimental conditions for electrodeposition of well adherent, compact and uniformly smooth coatings of refractory metals from solutions in fused salt electrolytes.

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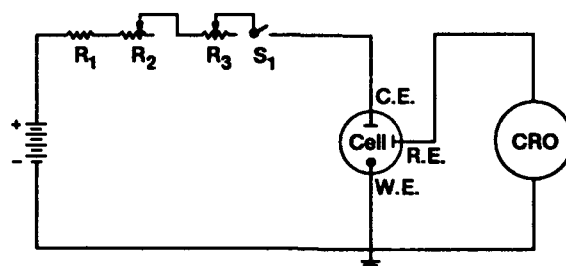


Figure 1.—A schematic circuit diagram for chronopotentiometry. W.E. - working electrode, C.E. - counter electrode, R.E. - reference electrode, CRO - cathode ray tube oscilloscope,  $S_1$  - switch,  $R_1$ ,  $R_2$ ,  $R_3$  - resistors.

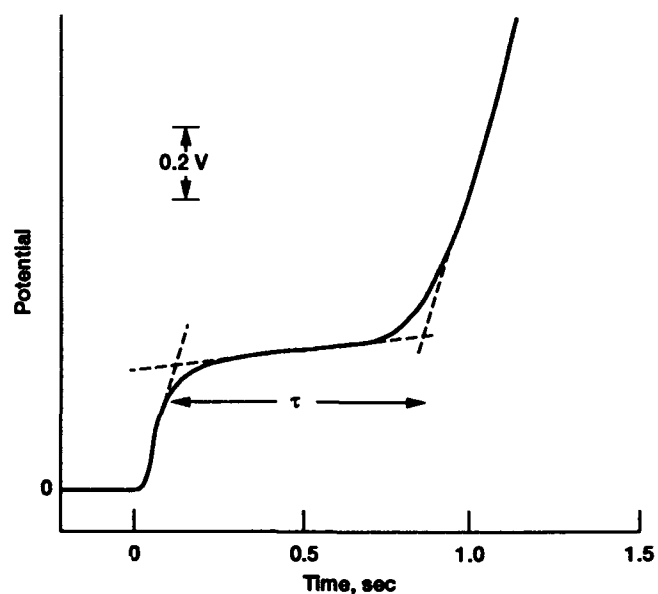


Figure 2.—A typical chronopotentiogram.

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